

REPORT DOCUMENTATION PAGE		Form Approved OMB No. 0704-0188
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1. REPORT DATE (11/26/02)	2. REPORT TYPE Progress Report	3. DATES COVERED (From - To)
4. TITLE AND SUBTITLE The Growth and Characterization of Metastable Free Radical Nanoclusters		5a. CONTRACT NUMBER F49550-04-1-0078
		5b. GRANT NUMBER 5-36808
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Tomas Baer, Roger E. Miller		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of North Carolina- at Chapel Hill Chemistry Department CB# 3290 Venable Hall Chapel Hill, NC 27599-3290		8. PERFORMING ORGANIZATION REPORT NUMBER 5-36808
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR 4015 Wilson Blvd., Rm 713 Arlington VA 22203-1954 <i>Dr Michael Berman/NA</i>		10. SPONSOR/MONITOR'S ACRONYM(S)
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION / AVAILABILITY STATEMENT <i>Approved for public release, distribution unlimited</i>		AFRL-SR-AR-TR-07-0222
13. SUPPLEMENTARY NOTES		

14. ABSTRACT The ultimate objective of the research was to form and study a wide range of radical complexes and nanoclusters in helium nanodroplets. The unique conditions present in the helium nanodroplets has enabled the production of interesting new systems that have not been observed using more conventional methods. Infrared laser spectroscopy was the primary tool for carrying out these studies. Among the systems investigated were the halogen HF and HCN complexes and the methyl radical HF complex, which forms the transition state in the F + CH ₄ reaction. The methyl HCN complex was also investigated.
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15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PEI Tomas Baer
a. REPORT Final report	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include code) 919-962-1580

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

The Growth and Characterization of Metastable Free Radical Nanoclusters

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This final report describes the research findings from the Miller group between 2005 and 2007, during which time the Miller group went from its pinnacle to its demise as a result of the sudden and tragic death of Roger Miller on November 6, 2005. During this difficult time, the Miller students continued to publish papers and completed the work required for their PhD degrees.

The major aim of this research project has been the study of weak interactions between open shell species and stable molecules. Much of our knowledge of intermolecular forces between stable molecules has come from the high-resolution spectroscopy of weakly bound closed shell complexes, and there is considerable promise that similar advances can be made for open shell complexes. Experimentally, the study of open shell reactive molecular complexes is more difficult than their closed shell counterparts due to the fact that their tendency to react must also be suppressed. The cooling provided by free jet expansion and matrix isolation is sometimes sufficient to stabilize complexes of this type. Recently, nanoscale liquid helium droplets have also emerged as a nearly ideal spectroscopic matrix for the study of highly metastable species, including the stabilization of pre- and post-reactive cluster systems. Such weakly bound complexes sample the long range van der Waals forces in the entrance and exit channel regions of the potential energy surface, which have recently been shown to strongly influence the reaction dynamics of $\text{Cl} + \text{HD}$ and the near threshold photodissociation of formaldehyde. Despite the fact that the magnitude of such orientational forces is usually very small in comparison with the energy of the transition state, the torque on the reactants at long range acts to deflect trajectories towards or away from the transition state.

The experimental approach has involved the use of helium nanodroplets. Helium droplets are formed by expanding ultra-high-purity helium gas through a 5 μm nozzle which is cooled to 18–22 K. The helium stagnation pressure was maintained at 50 bar, resulting in the formation of droplets with a mean size of 2500–6000 atoms. Radicals, such as halogen atoms or methyl radicals, were produced by pyrolysis and doped into the droplets using an effusive source while the stable molecule are added to the droplets downstream using a simple scattering cell. The documented growth of non-equilibrium structures in helium droplets is suggestive of a successive capture mechanism where dopants are pre-cooled before complexation occurs. The relative timescales for species finding each other in a droplet, to form a complex, and the rate of cooling are not precisely known. The cooling rate however must at least be competitive with coagulation in order to prevent annealing of previously formed metastable structures in the pick-up process. In much the same way, the energy gained due to the mutual interaction of two dopants must also be quickly removed and complexation will occur at low interaction energies comparable to the droplet temperature of 0.4 K. Therefore, complexes are typically trapped in a local minimum reflecting the approach geometry of the dopants. Of particular interest has been the finding that the low temperature often prevents rearrangement to the global minimum.

The infrared light from an F-center Laser (Burleigh FCL-20) or a PPLN-OPO (Linus Photonics OS-4000) interacts with the droplet beam using a linear multipass cell, designed to increase the effective interaction length. Excitation of the dopant inside the droplet leads to evaporation of approximately 600 helium atoms from the droplet, which reduces the on-axis beam flux reaching a liquid helium cooled bolometer. By mechanically chopping the laser and using phase-sensitive detection, the resulting beam depletion can be recorded as a function of the laser frequency to obtain the absorption spectrum. A set of Stark electrodes was aligned orthogonal to the laser interaction so that Stark and pendular spectroscopy could be performed. The DC electric field was oriented parallel to the laser polarization yielding $\Delta M = 0$ selection rules. Details on the calibration of the electric field are given elsewhere. In order to optimize conditions for the pickup of a single radical, the temperature of the pyrolysis source is adjusted, monitoring the percent dissociation of the precursor by probing both the X-M and X₂-M binary complexes, where X is the radical and M is the stable molecule.

Infrared laser spectroscopy of CH₃—HF in helium nanodroplets: The exit-channel complex of the F + CH₄ reaction

The helium nanodroplet method has been used to stabilize and spectroscopically study the CH₃--HF and CD₃--HF molecular complexes, corresponding to the exit channel complexes of the F+CH₄ (CD₃H) reaction. The infrared spectra indicate that the complexes have a hydrogen bonded, C_{3v} structure, in agreement with both *ab initio* theory and previous ESR studies. The rotationally resolved spectrum provides detailed information concerning the intermolecular potential and vibrational dynamics. A sixfold difference is observed in the vibrational relaxation times for the H-F stretch excited states of the CH₃--HF and CD₃—HF complexes, which we attribute to a near resonance between the HF and CH₃ vibrational modes, which is missing for H-F and CD₃, making relaxation in this latter complex much slower. This resonance could be facilitated by the ν_2 umbrella mode of CH₃, which may be coupled to the intermolecular coordinate. The intermolecular bending motion of the complex is also seen to have a significant effect on the vibrational frequency shift associated with the H-F stretch, which is qualitatively related to the substantial difference between the equilibrium and vibrationally averaged structures of this complex. These effects are clearly observed from the changes in the *A* rotational constants, dipole moments, and vibrational band origins with both vibrational excitation and isotope substitution. A one-dimensional model is presented, based on the intermolecular bending of the CH₃ and HF monomers in the complex, which gives only a qualitative agreement with the experiment. We conclude that a quantitative agreement will only be possible with theoretical calculations that simultaneously include several degrees of freedom. Only in this way will it be possible to extract detailed information on the potential-energy surface of this reactive system.

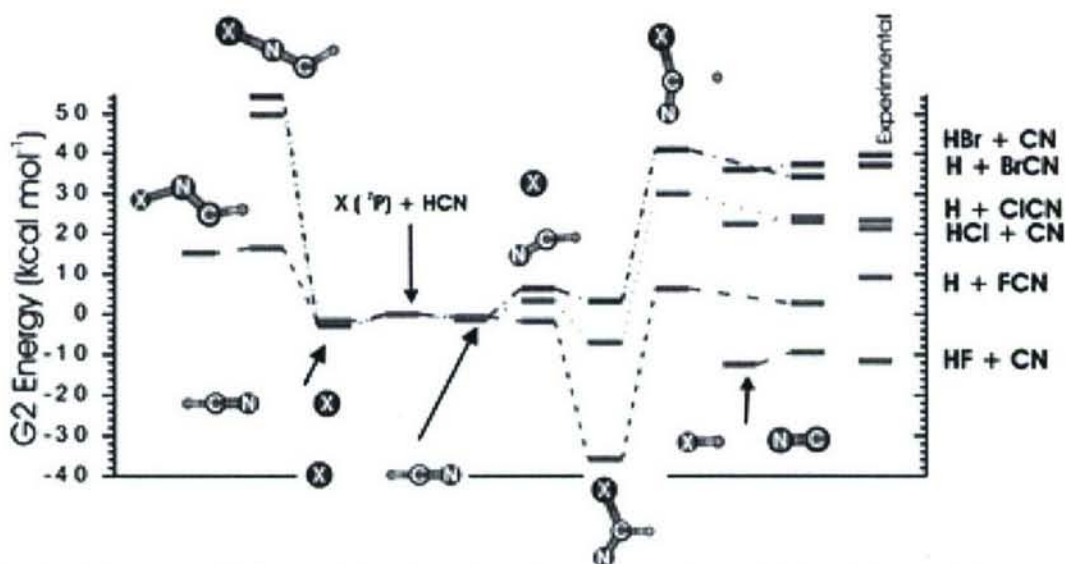
The twofold reduction of the experimentally measured *B* rotational constant, relative to the *ab initio* value, is typical of what has been observed previously for many different molecules in helium, which all suggest that the effective moment of inertia of a helium-solvated complex is larger than the gas-phase value, owing to the adiabatic following of the molecular rotational motion by some of the helium atoms. *Ab initio* calculations indicate that the binding energy of the complex is less than 2 kcal mol⁻¹, relative to the separated CH₃ and HF products.

These results suggest that future experiments on this system should be directed at measurement of the asymmetric C-H stretch on the methyl subunit, which should provide detailed information on the potential-energy surface in the exit channel of the F+CH₄ reaction.

A high-resolution infrared spectroscopic investigation of the halogen atom–HCN entrance channel complexes solvated in superfluid helium droplets

The reactions of halogen atoms with HCN have been the focus of extensive experimental and theoretical study, aimed at elucidating the role of the potential energy surface in determining the associated reaction dynamics. The CN group is often regarded as a pseudo-halogen, and thus there is interest in comparing the reaction dynamics of this tetra-atomic system with the analogous X–HY (X & Y = halogen atoms) triatomic systems. Interestingly, the long range interactions between XH + CN are expected to differ significantly from X + HCN due to the threefold degeneracy associated with the 2P ground state of halogen atoms, compared to the nondegenerate $^2\Sigma$ ground state of CN radicals, further lowering the symmetry of this hydrogen exchange reaction. Despite this, HCN is an ideal test case because the CN group is usually found to act as a single unit, but there is still considerable debate about whether or not the CN bond is a spectator to the dynamics of many different reactions. The additional degrees of freedom that the HCN molecule presents, open up many new channels of the potential energy surface that can be explored, and the X + HCN systems have provided benchmarks for the theoretical treatment of such multidimensional dynamics.

The potential energy surface for the X + HCN system is complex, which is characteristic of many open shell interactions. The figure shows both stable structures and dissociation paths.



The relevant stationary points of the X + HCN reactions calculated using the composite G2 method. Two reacted complexes in addition to two weakly bound entrance channel species are predicted. The HCNX products of chlorine and bromine atoms binding on the nitrogen end of HCN could not be stabilized in our calculations. The experimental heats of formation for the X + HCN → HX + CN and X + HCN → H + XCN reactions are taken from the literature. The photon energy used to study the pre-reactive X–HCN complexes is greater than the barriers to form HXCN, suggesting that it may be possible to photoinitiate this reaction.

The results of this combined theoretical and spectroscopic investigation of the halogen atom–HCN system shows that the potential energy surfaces for X + HCN are found to be

considerably more complex than for $X + HX$ due to the possibility of hydrogen atom abstraction and addition reactions. The lone pair on the nitrogen of HCN is also found to significantly alter the shape of the long-range potential energy surfaces, and for $X + HCN$, we find that the global minimum is a linear nitrogen bound geometry in contrast to the hydrogen bound global minimum for $X-HF$. A linear hydrogen bound $X-HCN$ complex is also predicted to be stable, however the isomerization barrier back to the global minimum is small. *Ab initio* calculations predict that for iodine and bromine significant barriers to the chemical reactions exist, and thus the entrance channel complexes should be quite stable when formed in a helium droplet. Both of the linear van der Waals isomers predicted by theory are observed experimentally for bromine and iodine atoms. Interestingly a HCN-Cl isomer was also observed whereas Cl-HCN was not. Since HCN-Cl is predicted to be the global minimum on the van der Waals potential, it could be that the isomerization barrier is simply too small to prevent Cl-HCN from rearranging to HCN-Cl. A second possibility is that the reactivity is enhanced on the hydrogen end of HCN, and Cl-HCN goes on to react to form HClCN. No entrance channel complexes were observed in the fluorine experiments, and we preliminarily interpret this as a result of reaction. The intermediate reaction product HFCN has been recently observed in an argon matrix; however, also in that work no pre-reactive complexes were observed. Preliminary searches for HFCN in this work in helium nanodroplets did not reveal this species. The photon energy used to study the CH stretching vibration of the entrance channel complexes is greater than the predicted barriers, suggesting that photo-initiation of the corresponding reactions could be possible. The unique asymptotic degeneracy of the multiple electronic states in the region of the entrance and exit channels for free radical-molecule complexes is found to give rise to fine structure in the observed spectra for HCN-Br and HCN-I.

Infrared-Infrared Double Resonance Spectroscopy of the Isomers of Acetylene-HCN and Cyanoacetylene-HCN in Helium Nanodroplets

This project differs from the others in that it deals exclusively with closed shell species. The goal here is the development of a double resonance technique to probe the vibrational dynamics of photoexcited molecules in helium nanodroplets. Using continuous wave tunable infrared (IR) lasers, the vibrational spectrum in the ground electronic state of many solvated species has been obtained. The vibrational spectrum is acquired by monitoring the helium droplet beam flux as the IR laser is tuned through the vibrational resonances of the molecule. In the vast majority of cases, the excited-state vibrational energy is removed by the droplet, resulting in the evaporation of helium and a corresponding reduction of the droplet beam flux. While there has been extensive work over the past decade to elucidate the mechanisms for the observed rotational and vibrational relaxation, there are still open questions, including what is the initial fate of a weakly bound hydrogen bonded or van der Waals complex upon vibrational excitation. A recent report on the IR-IR double resonance spectroscopy of the two HCN-HF isomers [Douberly, G. E.; Merritt, J. M.; Miller, R. E. *Phys. Chem. Chem. Phys.* **2005**, 7, 463-468] introduced a technique capable of addressing this question. As discussed below, the data was suggestive of a vibrational relaxation mechanism corresponding to vibrational predissociation of the complex similar to that observed for the linear HCN-HF complex in the gas phase. However, in the helium droplet, a matrix cage effect is observed, which results in the subsequent recombination of the fragments. As was observed for HCN-HF, if the fragments separate sufficiently within the droplet upon dissociation, an isomerization reaction occurs. While conformational isomerizations

have been studied in both rare gas matrices and in the gas phase, the use of helium droplets should prove to be an excellent and universal tool for studying the isomerization dynamics between metastable conformations on a molecular potential energy surface.

Instead of a photoinduced isomerization, it is easy to imagine the first infrared photon initiating a chemical reaction from a weakly bound entrance channel complex. The second, downstream laser in the IR-IR double resonance technique would then be perfectly suited to interrogate the reaction products. In addition, reaction intermediates trapped as result of the rapid cooling available could be probed with various infrared or optical spectroscopic methods. Herein lies the true promise of this and other double resonance helium droplet techniques, that is, the potential to completely characterize the global potential surface from reactants to products.

The study of the isomerization dynamics of the HCN-acetylene and HCN-cyanoacetylene binary systems, each having two stable isomers on their respective potential energy surfaces is an excellent example of this approach. For HCN-HCCH, vibrational excitation of either the linear or T-shaped complex resulted in positive double resonance signals on the other isomer, indicating an increase in the downstream population of the isomer not in resonance with the upstream infrared pump. Photoinduced isomerization was observed regardless of the identity of the vibrationally excited isomer. However, the downstream isomer ratios were found to be strongly isomer and vibrational mode specific. Excitation of the hydrogen-bonded C-H stretch of the T-shaped isomer lead to a downstream isomer ratio (1.3 to 1, linear to T-shaped) that was equivalent to the isomer ratio observed upon sequential pick-up by the droplet followed by condensation of the cold subunits. Pumping the bonded C-H acetylenic stretch of the linear isomer lead to a 3 to 1 downstream population ratio in comparison to 11 to 1 upon pumping the linear isomer's free C-H stretch. The ratios are consistent with vibrational predissociation followed by geminate recombination as the mechanism for isomerization. The rate of dissociation, controlled by the coupling of the intramolecular vibration to the intermolecular dissociation coordinate, apparently plays a critical role in determining the fraction of pumped complexes that become sufficiently separated within the droplet such that they overcome the barriers to isomerization.

In contrast to the isomers of HCN-HCCH, population transfer was not observed between the two linear isomers of HCN-HCCCN. Ab initio calculations of the long-range isomerization barriers show that, in order to randomize the initial relative fragment orientations, a separation of as much as 60 Å must be achieved following vibrational predissociation in comparison to ~20 Å for the isomers of HCN-HCCH. Apparently, the stronger long-range interactions (dipole-dipole) between the HCN and HCCCN fragments preclude rearrangement between the two linear isomers following vibrational excitation.

Publications resulting from the AFOSR funded project:

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3. G.E. Douberly, J.M. Merritt, and R.E. Miller, "Infrared-Infrared Double Resonance Spectroscopy in Helium Nanodroplets: Photo-Induced Isomerization" *Phys.Chem.Chem.Phys.* 7 (2005) 463-468.
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6. Myong.Y. Choi, G.E. Douberly, T.M. Falconer, W.K. Lewis, C.M. Lindsay, J.M. Merritt, P.L. Stiles, R.E. Miller, Infrared spectroscopy of helium nanodroplets: novel methods for physics and chemistry *Int. Rev. Phys. Chem.* 25 (2006) 15-75
7. Jeremy M. Merritt, Jochen Kuepper, Roger E. Miller, A high-resolution infrared spectroscopic investigation of the halogen atom-HCN entrance channel complexes solvated in superfluid helium droplets, *Phys. Chem. Chem. Phys.* 9 (2007) 401-416
8. Gary E. Douberly, Jeremy M. Merritt, and Roger E. Miller, Infrared-Infrared Double Resonance Spectroscopy of the Isomers of Acetylene- HCN and Cyanoacetylene- HCN in Helium Nanodroplets, *J. Phys. Chem. A.* (2007) in press